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**13. ABSTRACT (Maximum 200 Words)**

We report progress on the construction and testing of two high pressure organometallic chemical vapor deposition (HPOMCVD) reactors, real time feedback control of pulsed chemical beam epitaxy, reduced order model feedback control design, defect formation in heteroepitaxial growth of films, and remote plasma processing.

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# Modeling and Control of Advanced Chemical Vapor Deposition Processes: The Control of Defects in Mixed III-V Compound Heterostructures

**Final Technical Report**
for the period
July 1, 1995 – September 30, 2000

AFOSR F49620-95-1-0447

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## Objectives

- Integration of advanced methods of CVD with state-of-the-art mathematics to address fundamental scientific issues in the heteroepitaxy of mixed group II nitrides, phosphides and phosphonitrides on silicon and silicon carbide substrates, respectively.
- Utilization of advanced mathematics modeling and control theory to optimize existing state-of-the-art processing methods (e.g., chemical beam epitaxy (CBE) and remote plasma enhanced CVD and novel CVD processes (e.g., RTOMCVD at superatmospheric pressure) to (i) provide for real-time process monitoring and control, and (ii) establish conditions that are commensurate with the high throughput requirement of single wafer processing, and (iii) access processing conditions outside the reach of conventional CVD.
- These heterostructures have important potential applications in the context of : (i) uv detectors, green and blue light emitting devices and (ii) advanced ULSI technology. Although the markets associated with these potential applications are substantial, the exploitation of the commercial opportunities (i) and (ii) is restricted at present by challenging materials problems. New processing approaches are needed to meet this challenge.

## Status of Efforts

An interdisciplinary team of scientists from NC State University and Arizona State University has collaborated to achieve significant improvements in the understanding and control of advanced semiconductor thin film processing. The team comprised of Applied Mathematicians, Materials Scientists and Physicists has combined new control theory and a novel inexpensive and robust process monitoring method invented at NC State to create a tool for closed-loop process control. It's use has achieved substantially better control of composition and deposition rate as compared to conventional open-loop processing. In addition the team of scientists has designed and built a reactor for semiconductor thin film processing at elevated pressure of up to 10Mpa. Novel mathematical approaches have been introduced to extend control theory to the complex conditions of elevated pressure processing of semiconductors. Our reactor has been integrated with a state-of-the-art spectroscopic facility. It represents new infrastructure for thin film processing of materials with unique capabilities, such as processing of materials that exhibit high decomposition pressure at the optimum growth temperatures. The above work has focused on Group III nitrides and phosphides in the form of both thin film and self-assembled quantum dot structures that have well established as well as potentially new relevance to the DoD mission. For example these include sensing of chemical and biological agents, cock-pit displays with improved color coding and integration capabilities, new transistor technology for fast data processing in hostile environments, improved imaging and image reconstruction techniques, reduced order on-line sensing and feedback control in military systems development and robotics/sensors operating in remote hostile environments. Additional advancements have been made in faceting-induced

defects in heteroepitaxial growth, enhanced remote plasma processing and development of computational packages for reaction kinetics and precursor formation.

## Accomplishments and New Findings

Our DoD-MURI Research Program on Intelligent Design and Manufacturing in Electronics and Materials has accomplished significant advances in both Applied Mathematics and Materials Science and Engineering. It has allowed us to design, build and deploy new infrastructure enabling critical issues of the DoD Mission of Research to be addressed with methodologies not available anywhere prior to this effort. These can be summarized in the following seven achievements which are followed by seven more detailed summaries.

## Achievements

- Construction of two new systems for high pressure epitaxy: <u>First prototypes worldwide</u>
- Development of two <u>new robust methods</u> of real-time optical process monitoring for use in feedback control of epitaxy of high pressure
- Significant advances in understanding of defect formation/propagation in initial stages of group III nitride and phosphide epitaxy and surface-dipole mediated self-assembly of quantum dots on Si substrates.
- Successful application of principle of valence mismatch to control of fixed charge in MOSFET design.
- Computer aided design of HPCVD reactors.
- Implementation of nonlinear control and filtering in a PCBE system.
- Control and estimation methodologies for <u>nonlinear</u> HPCVD systems.

## 1. Initial Stages of Heteroepitaxy and Defect Formation

In the group of Prof. Mahajan at Arizona State research regarding initial stages of heteroepitaxy were investigated and extended to include nitride materials, such as, GaN and AlN. Wide bandgap nitride materials have received much attention in the past decade since the realization of blue and green light emitting diodes, high life time UV lasers and potential high power group III nitride transistors promise significant commercial gains in opening up well defined and understood markets. These device structures require high quality GaN templates layers mostly obtained by metal organic chemical vapor deposition (MOCVD). The growth process consists of a nucleation layer (NL) grown at low temperature (LT) and a thick (2-4 $\mu$m) GaN epitaxial layer grown at high temperature (HT), giving rise to the so called two-step process. There have been a number of studies on various aspects of this two step process for both GaN and AlN NLs. Also, a number of models for the origins of threading dislocations (TDs) in HT GaN epilayers have been proposed by different groups. However, a comprehensive experimental investigation has not been attempted.

Thus we have carried out experimental studies with two objectives: (i) to provide a clear and comprehensive understanding of the microstructural temporal evolution of the two NLs, and (ii) to investigate by TEM the origins of TDs at various initial stages of HT GaN deposition on LT GaN on annealed LT GaN and AlN NLs. The layers were grown on (00001) epi-ready sapphire substrates in a horizontal MOCVD reactor using trimethyl-gallium, trimethylaluminum and ammonia as precursors for Ga, Al and N, respectively.

The respective growth temperatures for the NL and HT-GaN epilayers were 530 C and 1030 C, respectively. For 1 hour growth of HT GaN films on LT AlN and GaN NLs, the width of rocking curves for the (0002) reflection are 250 and 460 arcsecs, respectively.

To investigate the metamorphosis of NLs upon HT annealing and dislocation origins during early stages of HT-GaN growth, film growth was terminated at the end of relevant `
growth steps and cooled down in the presence of ammonia.

Cross-sectional TEM images reveal that the as-grown GaN NL consist of facetted 3-D islands of predominantly zincblende structure. Tilted boundaries and stacking faults parallel to the interface are the main defects. Upon annealing the islands attain rounded appearance and are connected to each other by a thin interlayer. In comparison AlN NLs do not indicate 3-D islanding and are predominantly wurtzitic with a few tilt boundaries. Upon annealing the AlN NLs develop only surface undulations and remain smoother than the GaN NLs. The changes within GaN NLs upon annealing are ttributed to evaporation and redeposition. The growth initiation mechanisms for the HT GaN differ in that the rounded GaN islands transform into flat islands by step-flow growth from the step ledges on the sides of the annealed GaN NL islands. On AlN NLs HT-GaN step-flow growth is preceded by nucleation of GaN islands.

A number of researchers have shown that there are three types of TDs present in GaN epitaxial layers grown on c-plane sapphire. Thes are pure edge **a** type dislocations,

Mixed **c+a** type dislocations and pure srew **c** type dislocations. While it is ascertained that dislocations with ac type component are deleterious to device applications, it is still uncertain as to the effect of **a** type dislocations. A thorough investigation using weak-beam cross-sectional images of HT-GaN epilayers for various selected times into the overgrowth process show that twists and rotations between islands that coalesce may produce screw and mixed dislocations. However, coalescence is not a mechanism for the formation of **a** type dislocations that may be formed by glide and climb of BP dislocations. The flatter surface morphology of annealed AlN NLs therefore suggests that they may be preferred templated for HT-GaN growth. Thus we plan to conduct TEM and AFM investigations on the various stages of HT-GaN growth on AlN NLs, similar to the work done on GaN NLs. In addition we are investigating issues of phase separation and atomic ordering within InGaN and AlGaN layers with regard to

their structural stability under different temperature and pressure regimes. Optimized layers will then be used to grow device structures, such as, high electron mobility transistors (HEMTs). We are presently optimizing the growth of GaN on Si(111) using AlN as NL.

## 2. Research and Development for High Pressure OMCVD Reactors

In the first two years of this effort p-polarized reflectance spectroscopy (PRS), invented by Bachmann, Dietz and Miller at North Carolina State University (US Patent 5,552,327; September 3, 1996), has been developed into an inexpensive, robust method of real-time process monitoring. It was applied to studies of pulsed chemical beam epitaxy of GaP and GaP-InP alloys on silicon. Bachmann's work focussed in the last three years of this MURI effort on initial stages of heteroepitaxy. In a close collaboration with Prof. Mahajan, first at Carnegie-Mellon University, and later at Arizona State University, both the formation of perfect nuclei and mechanisms of subsequent formation of defects were investigated. Using PRS as real-time process monitoring tool, an incubation stage was identified in which the concentrations of constituent precursors to growth on the substrate surface built up to the critical supersaturation needed for nucleation. Its duration is designated as incubation time $\tau_i$. Onset of nucleation was also discernible by structure in the PRS signal. A third stage in the evolution of a contiguous epitaxial layer is epitaxial island growth that eventually results in coalescence, and a concomitant transition of the PRS signal into the interference oscillations characterizing steady-state growth at time $\tau_h$. By process interruptions at selected stages of epilayer evolution the features of nucleation and epitaxial overgrowth were investigated, using existing ex-situ atomic probe and high resolution transmission electron microscopy at both institutions. However, the difficult and very important cross-sectional high resolution transmission microscopy of our study were exclusively performed in the group of Prof. Mahajan. Prof. Mahajans students Mr. Narayanan and Mr. Westmeier came to NCSU to be trained in CBE growth and a student of Prof. Bachmann, Mr. Sukidi went to Carnegie-Mellon University to be trained in cross sectional high resolution electron microscopy. Both Mr. Sukidi and Mr. Narayanan have received their PhD degrees in Materials Science and Engineering. Dr. Sukidi is now gainfully employed at Motorola Company in Mesa, AZ. His work was continued by Mr. Vicent Woods in Prof. Dietz' group and by Ms. Sonya McCall in Prof. Bachmann's group. At NCSU, an ultra-high vacuum (UHV) scanning tunneling microscope was integrated with two independently pumped UHV antechambers for sample preparation and storage. Atomic resolution imaging od Si(111) 7x7 has been achieved in this system. As a result of the above studies several significant findings have been made:

1. Both $\tau_i$ and $\tau_h$ decrease with increasing temperature, and the cross-over in the surface kinetics from weakly temperature dependent growth to strongly

decreasing growth rate with increasing temperature occurs already in the island growth stage.

2. CBE growth establishes a substantial interfacial dipole for (001) and (111) interfaces. However, in addition to this contribution, surfactant effects to the modification of Wulff's law must be considered that control the shape of nuclei and formation of extended defects. Expanding the adhesion energy at the interface in terms of contributions of stress $\varepsilon$, surface dipole $q\bullet l$, and surface coverage $\theta$ by adsorbates, the modification of Wulff's law for heteroepitaxial nucleation takes the form

$$\frac{\sigma_{h_i k_i l_i}}{d_{h_i k_i l_i}} = \frac{\sigma_A - (\beta_o + \Delta\beta_\varepsilon + \Delta\beta_{q\bullet l} + \Delta\beta_\theta)}{d_{A/B}} = C.$$

Here the adhesion energy $\beta_0$ in the absence of stress, surface dipole formation and adsorbates is always positive and $\Delta\beta_\varepsilon$ is always negative. The surface dipole effect depends on the built-in field at the interface, that is on dopant distributions and the effect of adsorbates depends on the difference between surface reaction layers on the substrate and nucleus surfaces.

3. Unusually high aspect ratio vertical growth is observed for nucleation of metastable hexagonal GaP on Si(111) (see Section 1 above), which often terminates in a zincblende structure cap. Since changes of crystal structure for a material is associated with changes in band structure and energy gaps this result is important, as it opens avenues to quantum dot and vertical quantum wires incorporation band offsets as part of the structure.

Through the entire duration of our MURI Bachmann has collaborated with Dietz in studies of chalcopyrite structure semiconductors that are of interest to the U. S. Air Force in the context of countermeasures employing optical parametric oscillators. Toward the end of our MURI program this included interactions with Prof. Madarasz and Prof. Dimmock of the University of Alabama in theoretical evaluations of wave-guided non-linear optical interactions. It also included interactions with Prof. Hoffmann of Technische Universität Berlin and Dr. Ruderman, Dr. Zwieback and others of Inrad, Inc., Northvale, NJ, in defect studies regarding chalcopyrite structure materials.

In parallel to the above research, Bachmann collaborated with Banks, Kepler, Ito, Scroggs and Tran in evaluating initial choices of high pressure organometallic chemical vapor deposition reactors. This work led us to the selection of a specific design, a differentially pressure controlled (DPC) reactor, comprised of a fragile fused silica inner core horizontal channel flow reactor and a pressure bearing stainless steel shell with sensing and maintaining of the differential pressure between these two volumes by a differential baratron sensor and the flow of nitrogen into the outside steel chamber, respectively. Extensive work was devoted to the design of the flow control and gas flow switching panel, because pulsed supply of process gases and organometallic source vapors to the

reactor is an essential requirement of high pressure OMCVD. This is so, because the small mean free path of molecules, without separation of constituent source vapors, would invariably lead to homogeneous nucleation, and unwanted formation of powders rather than epitaxial growth on a heated substrate wafer. A considerable effort was made to assure process safety.

The reactor was used for studies of reactive formation of GaN interlayer that can serve as substrates in epitaxial growth of other group III nitrides. No significant enhancement of processing temperature of pure InN was possible with the DPC reactor. This is in agreement with results of x-ray diffraction studies under high nitrogen pressure published by Krukovsky et al. in 1998. Their data predict even higher nitrogen pressure requirements to suppress InN decomposition than indicated by the previously published data of McChesnay et al. (1972), which we used as the basis for the design of the DPC reactor. It confirmed the validity of our decision to build a second generation compact hard shell (CHS) reactor, expanding the pressure range to $10^7$ Pa. Design of this reactor was initiated by Bachmann in collaboration with Kepler and Banks in 1997 and completed in 1998. The reactor has been built and integrated with an optical diagnostics facility adding gas phase spectroscopy and flow characterization by laser light scattering techniques (see report of Prof. Dietz). PRS becomes difficult at high pressure due to density fluctuations in the gas phase and has been replaced in the CHS reactor by principal angle spectrocopy (PAS) that was introduced by Bachmann in 1998 and avoids the problems encountered by PRS. Therefore two new methods of optical real-time process monitoring PRS and PAS have been advanced and conceived, respectively, as part of this MURI effort. Because we have now access to the CHS reactor, we have honored a request by Battelle Northwestern Pacific National Laboratory (NPNL) for transfer of our DPC reactor and associated control equipment to this DOE facility. It will be used at an allocation of 50% time for serving needs of American industry. We have been told that their projects address problems that are unrelated to our goals, and that require only moderately elevated pressure. Therefore, we are satisfied that this technology transfer will both contribute to future developments in high pressure OMCVD, and enhance the impact of DOD's investment in design and construction of new infrastructure for advanced materials processing that we have carried out. Our own experimental work will continue with the CHS reactor with funding awarded to Profs. Dietz and Bachmann by NASA.

## 3. Semiconductor-Dielectric Interfaces

During the 5 year MURI effort the group led by Lucovsky has made major progress in investigation of interfaces in semiconductor devices. This progress and achievements include:
a) Direct experimental observation of dipoles at heterovalent interfaces using optical second harmonic generation.

In a collaboration with researchers in Professor H. Kurd's group at RWTH-Aachen, Germany, direct spectroscopic evidence for interfacial dipoles at Si-dielectric interfaces has been obtained by optical second harmonic generation, OSHG. This is a direct result of the selection rules for OSHG. Consider the Si-dielectric interface-dielectric system. Based on symmetry considerations, there is no OSHG signal from Si at the dipole level. There is however an allowed signal from any Si surface or interface. The non-crystalline nature of the dielectrics insures that any OSHG from these materials will be negligible, hence the strong relative sensitivity from the Si dielectric interfaces. Experiments conducted during this collaboration used to techniques to detect surface dipoles, measurements of: i) the azimuthal asymmetry of the OSHG signal as a function of step angle of vicinal (off-axis) wafers, and ii) the spectroscopic response of the OSHG signal. Results were internally-consistent and gave different interface dipole resonance energies for $Si-SiO_2$, $Si-Si_3N_4$ and Si-mono-layer $N-SiO_2$ interfaces.

The same approach has been extended to heterovalent interfaces between Si and GaP, and isovalent interfaces between GaN and GaAs involving polar surfaces of the III-V compounds. For the Si-GaP system, the interface contribution can be observed by choosing a polarization condition in which the bulk signals are suppressed. For the GaN-GaAs system, there is a lattice mismatch that leads to terminal N atoms on the GaN side of the interface. The surface orbitals are doubly occupied by electrons, leading to a dipole moment that shifts the resonance energy.

b) Models for interface dipole formation.

Interface dipoles have been calculated in two ways, using either i) an empirical model based on bond ionicity, or ii) a quantum chemistry calculation. The two methods give essentially the same interface dipoles and provide semi-quantitative agreement with the experimental results identified above.

c) Preparation and characterization of $Ge-SiO_2$ interfaces.

Interfaces between Ge and its native oxide $GeO_2$ have previously been shown to be highly defective, and not useful for any device applications. The direct deposition of either $SiO_2$ or $Si_3N_4$ onto Ge surfaces gave highly defective interfaces as well, presumably due to the formation of either $GeO_2$ or a Ge nitride alloy. Metal oxide semiconductor (MOS) structures were made by alternative technique in which the Ge dielectric interface was formed by remote plasma-assisted oxidation with and without monolayer interface nitridation. The MOS capacitors were completed by remote plasma-assisted deposition of $SiO_2$, under conditions in which any subcutaneous oxidation of the Ge substrate should have been suppressed by the interfacial oxidation step. MOS devices with and without the interface layers were compared. In all instances, the interfaces were highly defective compared to $Si-SiO_2$.

d) Preparation and characterization of Si-dielectric interfaces.

The scaling of silicon integrated circuits to smaller in-plane lateral dimensions of individual devices to increase speed and reduce cost through higher packing densities requires that insulating oxides and nitrides other than non-crystalline or amorphous $SiO_2$ be incorporated into the gate stacks of field effect transistors, FETs. These replacement insulators must have dielectric constants, k, significantly larger than that of $SiO_2$, e.g., in the range of 10 to 30, in order to increase the gate dielectric capacitance and thereby provide a sufficiently high

density of channel charge under operating bias voltages to meet current drive requirements. The increased physical thickness associated with the higher values of k must reduce tunneling currents for the same effective capacitance as referenced to an $SiO_2$ film. Finally, the alternative dielectrics must also have electronically-active defect densities in the bulk, and at interfaces with crystalline Si that are respectively the same or less than those of thermally-grown $SiO_2$ and Si-$SiO_2$ interfaces.

There are several research issues regarding replacement dielectrics. The focus of our activities has included four significant limitations on the performance of high-k alternate gate dielectrics that derive from inherent relationships between i) chemical bonding and physical properties, and ii) device operation. These are interfacial band offset energies, thermal stability against chemical phase separation, coordination dependent dielectric constants, and interfacial fixed charge. Using remote plasma-assisted deposition with upstream plasma excitation of an $O_2$/He mixture, and downstream injection of Si and/or metal atom metal organic precursors, interfaces between Si and $Ta_2O_5$, $Al_2O_3$ and $ZrO_2$-$SiO_2$ (Zr silicates) alloys could be formed. Maximum processing temperatures before the onset of chemical phase separation and/or crystallization were obtained from Fourier transform infrared (FRIR) spectroscopy, X-ray diffreaction (XRD) and high resolution transmission electron microscopy (HRTEM) imaging. Suppression of interfacial reactions during deposition has been determined by in-line Auger electron spectroscopy (AES). Based on capacitance-voltage (C-V) measurements on MOS capacitors with different dielectric thickness, fixed charge in excess of $5 \times 10^{11}$ $cm^{-2}$ was present at all of the interfaces studied. This is sufficient to shift threshold voltages of field effect transistors, and to degrade channel transport properties for both electrons and holes. The sign of the charge correlates with the bonding chemistry of the metal oxide or silicate, being negative for $Al_2O$ and positive for $Ta_2O_5$ and the $ZrO_2$-$SiO_2$ (Zr silicates) alloys.

e) Bonding Constraints at semiconductor dielectric interfaces.

Based on our studies of i) $Si_3N_4$ and silicon oxynitride alloys, and ii) the metal oxides and metal silicates on Si(100) surfaces, it has been found that chemical bonding constraints are qualitatively different at these two types of Si-dielectric interfaces, but never-the-less lead to interface defects that will adversely effect device scaling based on substitution of deposited dielectrics other than $SiO_2$. In many instances, e.g., for devices with $Si_3N_4$ and silicon oxynitride alloys, and $Ta_2O_5$, the insertion of an ultra-thin nitrided plasma-grown $SiO_2$ layer provides a marked reduction in defect density, typically about two orders of magnitude from the $10^{12}$ $cm^{-2}$ to the $10^{10}$ $cm^{-2}$ level. However, these interfacial contribute about 0.35 nm of 'equivalent oxide thickness', or EOT to the total dielectric. This limits ultimate device scaling by reducing the physical thickness of the higher-k oxide or silicate by an thickness in nm, of the order of 0.9 k. This thickness reduction is typically equivalent to an increased direct tunneling current of more than three orders of magnitude.

A possible solution has been proposed for the alternative metal oxide and silicate dielectrics. This involves taking advantage of the unique networking bonding of Al atoms in $Al_2O_3$ and in aluminate alloys. These alloys are based on the $AlO_2^{1-}$ negative network forming bonding group, which is then combined with a positive network forming group, such as $TaO_2^{1+}$, as in $TaAlO_4$, or with more electropositive group III and IV atoms such as Y and La, and Zr, and Hf, in

stochiometric compositions, including $Y(La)(AlO_2)_3$ and $Zr(Hf)(AlO_2)_4$. The effects of statistical fluctuations in the neutral interface bonding aluminate alloys or compounds on channel transport have yet to be determined. This approach can be extended to compound semiconductors by using ionic interfacial layers as for example $Ga_2O_3$ on GaN to provide a chemical bridge between the polar semiconductor face, and the metal oxide. silicate, or aluminate dielectric.

## 4. Real-Time Sensing and Control in Thin Film Growth

During the past 5 years Dietz and Ito have led a team conducting research supporting the development of real-time optical monitoring of thin film growth processes and demonstrated closed loop process control, using the thickness and compositional controlled growth of $Ga_{1-x}In_xP$ as an example. During this research program the team developed p-polarized reflectance spectroscopy (PRS) as a new method for real-time process monitoring. PRS has been applied to characterize the heteroepitaxial nucleation and overgrowth process as well as to follow thickness and composition and steady-state growth. During heteroepitaxial $GaP/Ga_xIn_{1-x}P$ growth on Si under pulsed chemical beam epitaxy (PCBE) conditions, the surface is periodically exposed to metalorganic precursors, which causes a periodic in composition and thickness altered surface reaction layer (SRL). The control of a growth process using the optical signature from the SRL that feeds the underlying growth has been implemented using instantaneous simulation and prediction of the surface chemistry and its link to the optical properties of the outer most layer in a multilayer medium. For this, a reduced order surface kinetics (ROSK) model was developed that describes the growth process with a mathematically reduced number of surface reactions equations. Parabolically graded $Ga_{1-x}In_xP$ heterostructure wells were grown under open- and closed-loop conditions that demonstrated that the on-line estimate of growth rate and composition provided by the PR probe adjusts to the nonlinearity in growth kinetics present in our system and provides better tracking to the desired composition and thickness profile.
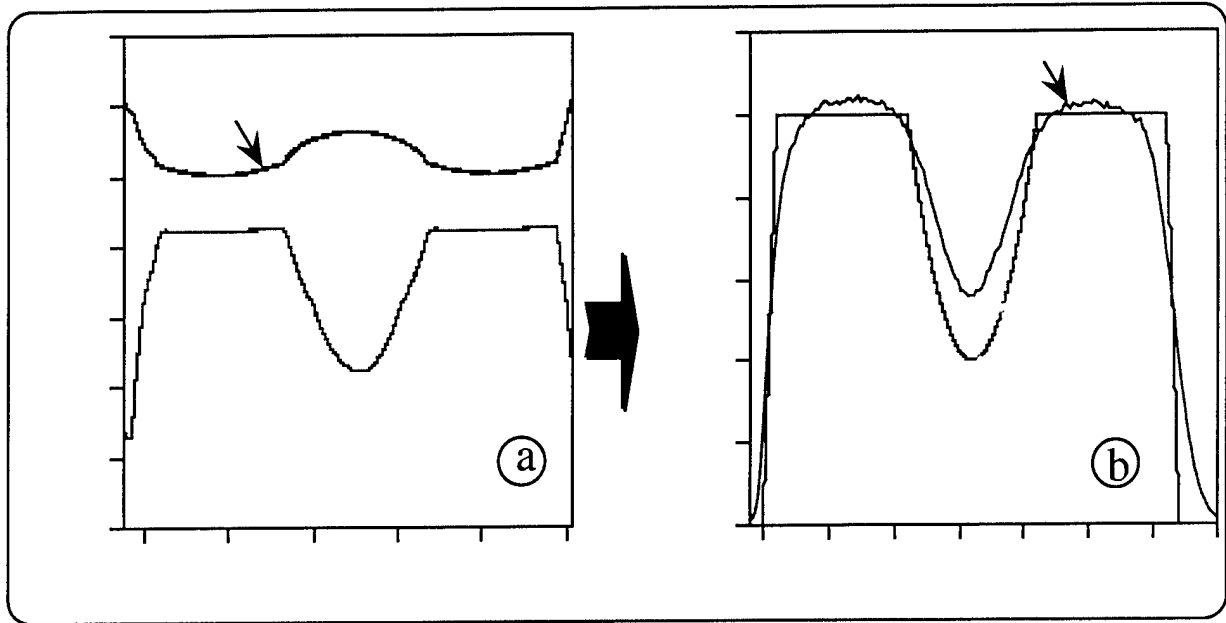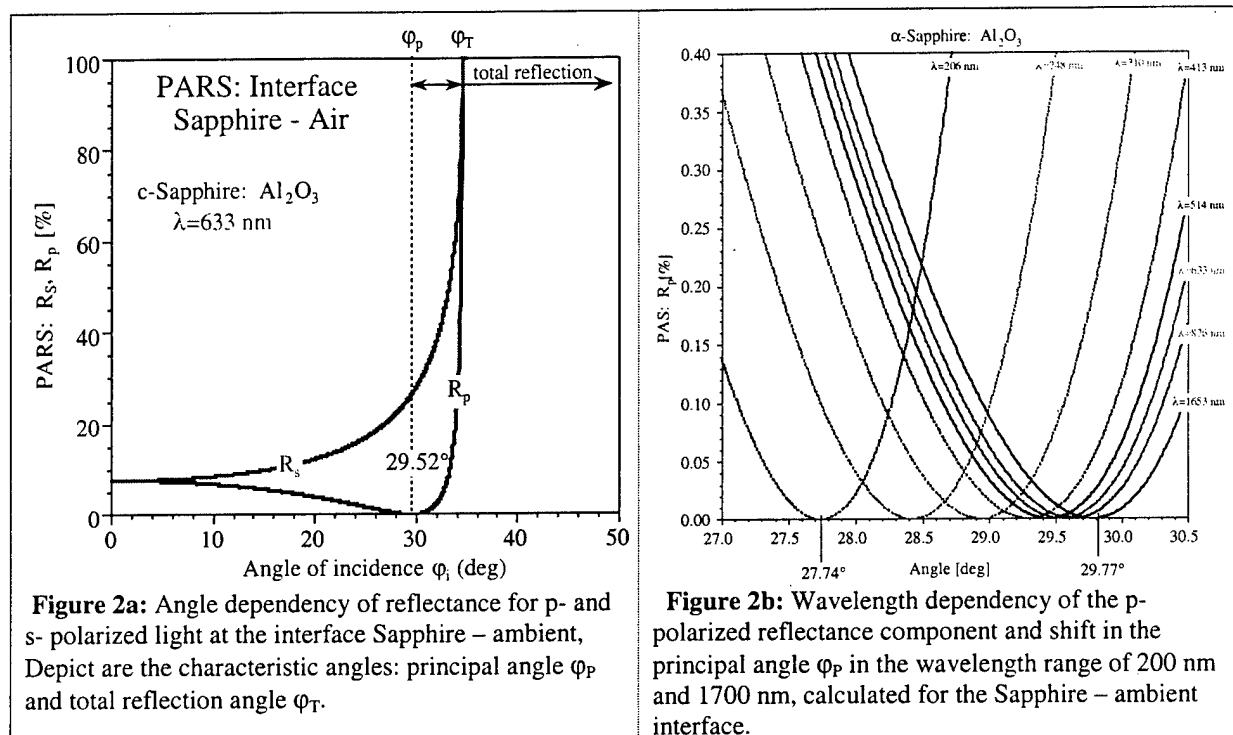
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Figure 1:    Closed-loop control of a parabolic Ga1-xInxP growth profile  a) Adjustment of precursor flux during close-loop control to achieve composition and thickness target. b) Ex-situ SIMS depth profile analysis for a parabolic graded $Ga_{1-x}In_xP$ heterostructure grown under close-loop control.

The simulation of the surface reaction kinetics was challenged by the limited experimental input parameter available to discriminate between molar surface constituents. With help of a DURIP equipment grant, we were able to implement a tunable laser system, capable to obtain wavelength specific optical response parameters. This allows us to discriminate between different surface constituents and to expand our surface reaction kinetics model to be more specific which wavelength response is taken for process control.

For low-pressure growth processes the PRS response demonstrated a h¹ɡʰ signal-to-noise ratio, which allows the monitoring of surface constituents with sub-monolayer resolution. At higher ambient pressures in the growth reactor, we encountered signal fluctuations and distortions related to gas flow variations and the temperature gradient over the substrate surface. The loss in sensitivity led to the development of principal angle reflectance spectroscopy (PARS), which has been implemented in the newly constructed high-pressure, compact hard shell (CHS) reactor together with a variety of gas phase characterization techniques (see annual MURI report 1999/2000).  As schematically depicted in Figure 2a, PARS utilizes p-polarized light impinging the substrate-ambient interface near the principal angle $\varphi_P$.  The angle of total reflection, $\varphi_T$, is approximately 5 deg above $\varphi_P$.  The wavelength dependency of the principal angle is shown in Figure 2b with a calculated shift of more than 2 deg in the wavelength range of 200 nm and 1700 nm.  The temperature shift is in the order of 0.2 deg between room temperature

(RT) and 1000°C. Utilizing these two angles of incidence, two independent but complementary measurements can be performed at the same time.



**Figure 2a:** Angle dependency of reflectance for p- and s- polarized light at the interface Sapphire – ambient, Depict are the characteristic angles: principal angle $\varphi_P$ and total reflection angle $\varphi_T$.

**Figure 2b:** Wavelength dependency of the p-polarized reflectance component and shift in the principal angle $\varphi_P$ in the wavelength range of 200 nm and 1700 nm, calculated for the Sapphire – ambient interface.

For flow dynamic analysis as well as for studies of gas phase reactions, optical access ports are integrated perpendicular to the flow axis. Rayleigh scattering will be utilized in detecting turbulent flow. At low pressure and high temperature, where thermal motion is described by the Maxwell-Boltzmann distribution, a Gaussian line shape is observed for the Doppler-shifted intensity. However, at high pressure, the Gaussian line shape is altered by superposition of Lorentzian components associated with collective motions, such as, thermal diffusion and Brillouin scattering from acoustic waves. Because of the relatively small solid angle for collection of incoherently scattered radiation we added absorption spectroscopy at specific energies in resonance with vibrational-rotational signatures for the most important molecular fragments diffusing toward the surface of the growing film. Simultaneous monitoring of Raman scattering, absorption spectroscopy, Rayleigh-Brillouin scattering, and PARS, provides information on temporal and spatial temperature fluctuations, and variations of concentrations of specific constituents in the vapor phase. In conjunction with the results of process simulations these experimental data provide all necessary experimental input needed for advanced flow and gas reaction kinetics simulations as well as for process control.

## 5. Numerical Methods for Control

Ito and associates carried out fundamental research on control methodology for distributed systems. These include:

(1) Development of numerical methods for constructing the optimal feedback synthesis for the nonlinear regulator problem. The optimal feedback law is determined by the dynamical programming principle. However a direct integration of the dynamic programming equation suffers the curse of the dimensionality. We utilize the optimality relationship between the Pontragyin maximum principle and the dynamic programming principle to overcome the difficulty. Our construction method is based on the solutions to the two-point boundary value (TPBV) problem for each initial condition at selected gridpoints. That is, the solution of the TPBV solution corresponding to each gridpoint provides the optimal feedback law at the gridpoint. Then we use interpolation methods to approximate the optimal feedback synthesis.

To this end we developed an efficient and accurate numerical integration method for the TPBV problem based on Runge-Kutta-Gauss method. Convergence properties and rate of convergence of the proposed method are established. We also developed an interpolation method based on the bi-harmonic Green's function. We demonstrated the feasibility of our proposed construction method using test examples. Our test examples include a regulator problem for the Lorenz system as well as a reduced-order control problem from control of the Navier-Stokes equation.

(2) Analysis of the asymptotic stability of the receding horizon control principle. The receding horizon control problem involves the successive solution to the fixed finite time horizon optimal control problem. It provides a feedback synthesis since the control law is determined as a function of the initial condition on each horizon. If we select our time horizon sufficiently small, then this offers very efficient control synthesis. It is very important to analyze the asymptotic stability and its performance. We showed that if the terminal cost is chosen to be a control-Liapunov function, then the resulting closed loop is asymptotically stable and we can obtain an upper bound estimate of the performance index. Our result is applied to a general class of nonlinear control systems governed by PDEs. The receding horizon control principle provides an alternative to reduced-order control synthesis as a real-time control synthesis for nonlinear infinite dimensional control systems.

## 6. Reduced Order Methodology and Feedback Controls

In continuing development of the proper orthogonal decomposition (POD) method as a reduced order method for the modeling and synthesis of

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compensator-based feedback controls for the high-pressure chemical vapor deposition (HPCVD) reactor, Banks, Tran, Kepler and Beeler have made significant progress as well as important findings in the following areas:

(i)    Reduced Order Modeling. We have successfully demonstrated a computational implementation of reduced order feedback control of pulsed HPCVD III-V film growth that includes the transport of time dependent multiple species with linear gas phase reactions (Arrhenius reactions). The feedback control was implemented using a reduced order state estimator based on partial state observations of the fluxes of the Group III and Group V reactants at the center of the substrate. These observations are compatible with current p-polarized reflectance spectroscopy (PRS) sensing technology that is being utilized by our team. The controls are designed so that the output fluxes track time dependent target fluxes, similar to the pulsed sources currently employed for HPCVD film growth. The POD-based design method allows us to reduce the order of the system by a factor of 100 with respect to a standard finite element representation (i.e., from a system of 2159 finite element equations to 19 POD equations). In addition, to test the performance of the reduced order control/compensator design in the actual physical system, we applied the reduced order tracking control to the full finite element system with the reduced order state estimator. Our numerical simulations indicate that substantial control authority is still achieved with the reduced order model design. The positive results on the linear system (our work on the nonlinear system is reported below) suggest that real-time feedback control with partial state observations is a feasible goal for HPCVD reactors operating in steady state flow regimes with pulsed vapor reactant inputs.

(ii)   Deposition Process Modeling. The understanding of thin film growth processes and their control requires the development of surface-sensitive real-time optical characterization techniques that are able to provide insight into the surface reaction kinetics during an organometallic deposition process. These insights will allow us to move the control point closer to the point where the growth occurs, which in a chemical beam epitaxy process is the surface reaction layer (SRL), built up of physisorbed and chemisorbed precursor fragments between the ambient and film interface. In this context, we have developed a reduced order surface kinetics model using generalized reaction rate parameters to describe the decomposition kinetics of the organometallic precursors tributylphosphine (TBP), triethylgallium (TEG), and trimethylindium (TMI) during the low temperature growth of epitaxial $Ga_{1-x}In_xP$ heterostructures on Si(001) substrates by pulsed chemical beam epitaxy (PCBE). The resulting set of coupled, nonlinear differential equations that describe the surface reaction

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kinetics of our three precursor pulses provides information about the dynamics of molar concentrations of precursor fragments stored in the surface reaction layer and their incorporation into the growing film. The link between the unknown parameters and PRS measurements was identified as we fitted experimental data sets with the unknown parameters involved in the surface kinetics. The results showed that the mathematical model can be effectively used to describe both the small- and large-scale features of the experimental data and to accurately model the deposition process.

(iii)    Nonlinear Observer and Feedback Tracking Control. As mentioned above, to move the control point closer to the point where the growth occurs, which is the surface reaction layer, one has to couple the linear, time-dependent species transport with the nonlinear deposition process. This results in a system of nonlinear dynamical equations describing the transport of species from the inlet to their incorporation into the growing film. For the film thickness tracking control problem with partial state observations, we have developed new methodologies for nonlinear observer and nonlinear feedback tracking control. These methods, which are based on the "state-dependent Riccati equation", are not only applicable to the HPCVD reactor problem but also to a wide class of nonlinear systems that are important in practice. Moreover, these new nonlinear observer-based feedback tracking controls are computationally easy implementable as well as very efficient. Numerical experiments with these new techniques on several selected example problems show significant control authority and improvement (in places dramatic improvement) when compared to previously established control methods including the linearized system-based methods.

We have carried out specific 3D simulations of the new CHS reactor. In which we simulated steady state flow of the nitrogen carrier gas at 1 and 10 atm. Temperature modeling includes conductive heat transport in the plane of the reactor (alumina) walls, radiative heat exchange between wall surfaces, and conductive heat loss to the (cooled) outer walls of the reactor. Transport of reactants was also simulated at 1 and 10 atm for trimethylgallium (TMGa) and phosphine (PH3) source materials. Reactions included decomposition of TMGa to dimethylgallium (DMGa) $Ga(CH_3)_3 \rightarrow GaCH_2 + CH_3$, decomposition of DMGa to monomethylgallium (MMGa) $Ga(CH_3)_2 \rightarrow GaCH + CH_3$, and decomposition of phosphene to $PH_2$ $PH_3 \rightarrow PH_2$ H or PH $PH_3 \rightarrow PH + H_2$ Reaction rate constants were adjusted to reflect the high pressure limits.

The transient simulations were used to create POD modes for reactant transport in the new 3D CHS reactor. These POD modes are presently being used in numerical investigations on the use of proper orthogonal decomposition (POD)

techniques as a reduced basis method for computation of feedback controls and compensators in the CHS reactor. Numerical implementation of the model-based feedback control requires a nonlinear reduced order state estimator based on partial state observations of the absorption of light traversing the reactor. Methods have been developed to numerically implement the nonlinear absorption state estimation using a reduced order model based on POD modes.

## 7. Summary of Achievements
Summary of significant computational achievements, efforts and findings during the 5 year MURI effort.

### Computational Achievements
- Achieved major impact with computer simulations on reactor design. A team at N.C. State University composed of material scientists, physicists, and applied mathematicians, have used computer simulations as a fundamental design tool in developing a new prototype high pressure organometallic chemical vapor deposition (HPOMCVD) reactor for use in thin film crystal growth. The advantages of such a reactor lie in improved advanced technology products involving exotic materials with high thermal decomposition pressures and increased control over local stoichiometry and defect formation.
Early design of the HPOMCVD reactor dramatically evolved long before any physical reactor was built. These efforts took place over a period of approximately 2 years and involved close daily collaboration between the material scientists, physicists, and applied mathematicians. Mathematical modeling and computer simulation were the essential tools in the design effort. The rapid progress and substantial savings to date constitute a dramatic and powerful argument for the modeling and simulation design approach in this and other areas of emerging technologies.
- Use of computer simulations to create a reduced order model. Accurate simulations of the horizontal reactor have been used to provide input data necessary for the construction of a reduced order model for real-time control that captures the underlying physical processes. The modeling of reactant transport in HPCVD reactors is more complicated than in the case of low pressure CVD reactors. In general, a full mathematical model describing transport processes in (HPCVD) systems is given by a system of nonlinear partial differential equations representing the continuity, momentum, energy, and species equations of state. Numerical simulations and control designs of such systems using finite element, finite difference, or spectral methods lead to very large systems of ordinary differential equations rendering real-time full model-based feedback control design infeasible. Substantial dimensional reduction can be realized using the method of POD to more efficiently represent the system data. Application of the method of principal orthogonal decomposition (POD) to the reactant transport data has produced considerable

dimensional reduction (10 POD modes instead of 47,000 finite element nodal values) making implementation of real-time model-based feedback control feasible

- We have demonstrated a computational implementation of reduced order feedback control of pulsed HPCVD III-V film growth involving the transport of multiple species with linear gas phase reactions. We implement feedback control using a reduced order state estimator based on observations of the fluxes of the Group III and Group V reactants at the substrate center. These observations are compatible with current PRS sensing technology. The controls are chosen so that the output fluxes track time dependent target fluxes, similar to the pulsed sources currently employed for HPCVD film growth. Because the control values must be constrained to be positive (positive mass fraction) the resulting truncated control is suboptimal, but the reduced order model design is still capable of substantial control authority. These results suggest that real-time feedback control with partial state observations is a feasible goal for HPCVD reactors operating in steady state flow regimes with pulsed vapor reactant inputs.

Recent work has extended the implementation of the model-based feedback control to include a nonlinear reduced-order state estimation based on partial state observations of the absorption of light traversing the reactor. Methods have been developed to numerically implement the nonlinear absorption state estimation using a reduced order model based on POD modes.

**Experimental Achievements**

- P-polarized reflectance spectroscopy (PRS), invented at North Carolina State University, has been developed into an inexpensive, robust method of real-time process monitoring for process control. An experimental data base for the growth of $Ga_xIn_{1-x}P/GaP$ heterostructures by chemical beam epitaxy has been established and analyzed to derive the set of process parameters needed for process simulations. The predicted desired process evolution, based on real-time process simulations, was compared to the actual process evolution, derived from PR measurements on the basis of virtual interface theory, to detect and correct deviations. Significant improvements in control were obtained as compared to open loop control.

- Investigations of early stages of heteroepitaxy of GaP on Si have revealed self-assembly of perfect quantum dots for a nearly lattice-matched materials combination for polar/non-polar interface orientations. We attribute this to interfacial dipole formation. Also, we have observed the formation of metastable wurtzite structure GaP quantum dots on Si(111).

- Investigations of group III-nitride growth on c-plane sapphire substrates show substantial interface roughening of low temperature AlN and GaN nucleation layers (NLs) upon annealing. While subsequent high temperature GaN growth proceeds on GaN NLs by step flow, GaN growth on AlN NLs requires nucleation. Yet surfaces covered by flat topped assemblies of GaN form faster

on AlN than on GaN NLs. Analysis of formation of threading dislocations (TDs) revealed that TDs containing detrimental c-segments are formed in early stages of high termperature epitaxy, and are related to rotations and twist of GaN islands with regard to each other. Pure edge character NLs are formed in later stages of high temperature GaN growth by dislocation interactions and climb, but are not considered as detrimental to device fabrication.

- Two high pressure organometallic vapor phase epitaxy reactors were designed and built. The first prototype reactor was built to cover a pressure range p<1 Mpa, which turned out not to be sufficient to achieve a significant increment in processing temperature for the growth of InN. The second extends the operating pressure to 10Mpa and has been integrated with the optical monitoring facility for the characterization of flow dynamics by light scattering and real time monitoring of gas phase composition and surface reactions awarded to us by a DURIP grant in 1998, which is now operational. Upon request by Battelle Northwestern Pacific Laboratory a technology transfer has been negotiated that moves our first prototype reactor to this institution for serving at 50/50 time sharing basis needs of American industry and DOE internal research. Our own experimental work will continue with funding awarded by NASA.

**Personnel Supported** (with current locations for students and postdocs after leaving NCSU)

H.T. Banks, K.J. Bachmann, G. Lucovsky, K. Ito, H.T. Tran, N. Dietz,. M. Kushner, H. Yang, J.S. Scroggs, S. Mahajan, M. Fang (Tomphson), C. Hoepfner (Spire Inc.), G.M. Kepler (CIIT), I. Lauko (U. Wisconsin, Milwaukee), H.V. Ly (Cal. State at Fullerton), G. Pinter (U. Wisconsin, Milwaukee), S. Ravindran (NASA), R. del Rosario (U. Phillipines, Manila), F. Schienle (Aixtron), F. Wang, S. Beeler (PhD, December, 2000; NASA Langley Res. Ctr.) D. Cronin, C. Harris (MS, July 1999), E. Keiter, R. Kinder, R. Johnson, S. LeSure, J. Lu, S. McCall, V. J. Narayanan, E.H. Sanchez, J. Schroeter (PhD, December 1998; EPA), T. Simon (PhD, March 1999; Intelligent Sys.), D. Stephens, N. Sukidi (PhD, March 1998; Motorola), A. N. Westmeyer, D. Wolfe, V. Woods (MS, December 1999), N. Young, D. Zhang

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## Interactions and Presentations

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to Experiment", SIAM Mathematical Aspects of Material Science, Philadelphia, PA, May, 1997.

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30. M.J. Grapperhaus and M.J. Kushner, "Applications of Plasma Equipment Modeling to Ionized Metal PVD", Materials Research Corp.; Aug., 1997.

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39. H.T. Tran, "Inertial Manifolds Based Feedback Control for Liquid Film Flows", Karl-Franzens-Universität Graz, Institut für Mathematik , Colloquium Talk, January, 2000

40. H.T. Tran, "Reduced Order Based Compensator Control of Thin Film Growth in a Chemical Vapor Deposition Reactor", University of The Philippines, Manila, Department of Mathematics, Colloquium Talk, June, 2000.

41. H.T. Tran, "Reduced Order Based Compensator Control of Thin Film Growth in a Chemical Vapor Deposition Reactor", Workshop on Proper Orthogonal Decomposition and Its Applications; (45 minutes invited talk), , May 2000, Graz, Austria.

42. H.T. Tran, "Model Reduction and Feedback Control of Nonlinear Infinite Dimensional Systems",2000 SIAM Annual Meeting; (30 minutes invited talk in an invited minisymposium), July 2000, Rio Grande, Puerto Rico.

43. H.T. Banks, "Reduced Order Control of CVD Reactors", Oberwolfach, Germany, June, 2000.


## Transitions

Our research group, through the Kushner-led group at UIUC, collaborated with the microelectronics industry in the use of computer codes in the design of plasma processing systems. The MURI supported this activity by improving the capabilities of the models. The microelectronics industry has supported technology transfer activities by providing funding for both code development and for the actual university-interactions. Customers of thᵢ technology transfer include:

Semiconductor Research Corporation, Research Triangle Park, NC
Motorola Predictive Engineering Laboratory, Austin, TX
Lam Research, Fremont, CA
Applied Materials, Santa Clara, CA
Dupont Central R&D, Wilmington, DE

Power sources for direct energy weapons, remote controlled robotics and sensors have been identified (Star 21 Strategic Technologies for the Army of the Twenty First Century, National Research Council, Washington, DC, 1992, pp. 181-184) as a critical area that demands improvement of existing and development of new technologies. HPOMCVD opens up opportunities for the manufacturing of an improved $^{238}PuO_2$ fuel with hermetic composite encapsulation of individual fuel pellets. This will improve ease of handling and matching the fuel to specific applications, improve control of fuel temperature and may enable use of cheaper container materials. If DoD interest should exist, Dr. Timothy George of Los

Alamos National Laboratories would be a possible contact person. McDermott Technology, Inc. is a possible industrial partner.

Through a combination of mathematical design and experimental validation we have developed the first High Pressure Organometallic Chemical Vapor Deposition (HPOCVD) system for the pressure range between 1 and 6 atm. This reactor system has been transitioned to Battelle Pacific Northwest National Laboratory. The technology will be made available 50% of the time to US industrial researchers and 50% of the time to the Department of Energy internal research, to address problems of chemical vapor deposition that require access to above atmosphere pressure in the range of 1 to 6 atm.

Contact information:
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## New Discoveries Patents and Inventions

US Patent 5,552,237; September 3, 1996, for PRS.

## Honors and Awards

**Banks:**
Fellow of IEEE; University Professor and Drexel (Endowed) Professorship; SIAM Board of Trustees1997- present and Board Chair, 1999; IEEE-CSS Control Systems Technology Award, Kobe, Japan, December 1996; Distinguished Alumnus Award, Purdue University, May 1998; Fellow, Institute of Physics, 1999; Alumni Distinguished Graduate Professor, NCSU, 2000.
**Bachmann:**
Alcoa Foundation Distinguished Engineering Award, May 1997.
**Lucovsky:**
Fellow of AVC; Fellow of American Physical Society; University Professor.
**Mahajan:**
Fellow of ASM; The John Bardeen Award of TMS for excellence in research and leadership in electronic materials; The Albert Suavier Achievement Award of ASM for outstanding contributions in electronic materials and deformation behavior of solids.